Femtosecond interband hole scattering in Ge studied by pump-probe reflectivity

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Abstract

We have measured the transient reflectivity changes of bulk Ge after excitation with 140 fs laser pulses at 1.5 eV. The electron and hole dynamics are calculated using an ensemble Monte Carlo method. We find that the observed reflectivity changes are due to three main mechanisms: diffusion, band gap renormalization, and carrier dynamics, particularly scattering of light holes to the heavy hole band via the optical deformation potential interaction. Because of the unique band structure of Ge and the use of a reflectivity technique, we can isolate the role of the light holes with femtosecond time resolution. The Monte Carlo simulation (which uses an optical deformation potential for holes of d_0=46 eV) overestimates the scattering rate of light holes to the heavy hole band. The agreement can be improved when a lower value for the deformation potential (determined from theory or other experiments) is used.

For many years, femtosecond laser spectroscopy has focussed on III-V semiconductors and only a few picosecond studies [1–4] of Ge were conducted. This has changed recently [5–9], partly due to the arrival of the femtosecond titanium-sapphire laser and a revived interest in Ge and $Si_{1-x}Ge_x$ alloys as

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electronic and optoelectronic materials. Previous studies using femtosecond photoluminescence [8], transmission [5,9], and four-wave mixing [1,6] have focussed on carrier thermalization [8], electron dynamics such as intervalley scattering [6,8,9], band gap renormalization [9], diffusion [1,2], and hole thermalization [5]. The scattering of split-off holes to the heavy and light hole bands was observed by Woerner *et al.* [5], but the authors were unable to measure the scattering time within the time resolution of their experiment. In this work, we concentrate on a different facet of the hole dynamics, namely the scattering of light holes to the heavy hole band: Because of the unique band structure of Ge, the electrons scatter to the satellite valleys within about 100 fs, and therefore do not contribute to the Drude response measured in our reflectivity experiment. The remaining reflectivity signal is due to the light holes. Therefore, we are able to isolate and study the light hole population in Ge with femtosecond time resolution.

For a number of reasons, it is difficult to interpret the results of femtosecond laser experiments in semiconductors: (i) The initial distributions of the photoexcited electrons and holes are nonthermal. (ii) When the carriers equilibrate, the electron and hole temperatures are usually much larger than the lattice temperature. (iii) Many different processes affect the carrier population and therefore the observed spectra. In a typical experiment with bulk GaAs or Ge, the following processes have to be considered: (a) Free carrier, excitonic, Auger, and surface recombination; (b) lateral and vertical diffusion; (c) carrier cooling by emission of optical and acoustic phonons via the polar, piezoelectric, and deformation-potential interaction (only the latter is present in Ge); (d) intervalley scattering for electrons and interband scattering for holes; (e) carrier-carrier scattering; (f) screening of interactions at high carrier densities; and (g) band gap renormalization (BGR).

Since so many mechanisms have to be considered, comparison with experiments requires detailed numerical calculations. Typically, the ensemble Monte Carlo method is used [10,11]. The clever design of an experiment or choice of laser wavelength and material can also be used to isolate a single process. In the past ten years, the following processes have been studied in detail and are reasonable well understood: (i) In polar semiconductors, the electrons [12] and holes [13] cool by emission of longitudinal optical (LO) phonons (Fröhlich interaction). The observed reduction of the energy loss rate compared to theory is due to the generation of nonequilibrium LO phonons [14] (with a lifetime of 5 to 10 ps) and screening of the Fröhlich interaction [15]. Only the deformation potential interaction is responsible for cooling in Ge [3–5]. (ii) After laser excitation, the carriers diffuse [1,2] laterally (along the surface) as well as vertically (into the sample). Electrons and holes need to diffuse at the same rate (ambipolar diffusion) to prevent the build-up of an electric (Dember) field. (iii) In a pure, perfect Ge crystal with clean surfaces, the main recombination mechanism is the Auger effect [1]. (iv) In many-valley semiconductors, the electrons (created near the center of the Brillouin zone) scatter to satellite valleys near L and X within about 100 fs [6,8,9]. (v) The band gaps shrink due to exchange and correlation effects [16]. The most convenient way to observe this shrinkage, known as band-gap renormalization (BGR), is with CW or time-resolved photoluminescence measurements [17].

In contrast with these observations (which mainly deal with the relaxation and dynamics of electrons or electron-hole pairs and cooling of holes), little experimental evidence exists to single out the role of the holes in an undoped crystal, particularly the scattering between the different hole bands. In a Monte Carlo simulation, the holes need to be considered in a number of ways: (i) The complex valence band structure [18] (heavy, light, and split-off holes, warping of the bands) determines the initial electron distribution. (ii) Holes scatter with electrons, which is best described using a molecular dynamics approach. At high densities, electron-hole scattering is very efficient and the hole-phonon interaction is essentially unscreened [14]. (iii) Since holes are created in three different bands, they may scatter between them. This is analogous to intervalley scattering for electrons. The main difference is, however, that the scattering wave vector is much smaller. Therefore, the usual pseudopotential approach [19] may not be appropriate in this case.

Interband hole scattering is an intrinsic component of electric transport in p-type semiconductors. Classical treatments by Wiley [18] and Conwell [20] have studied this mechanism in great detail. However, since so many other factors (most importantly ionized impurity scattering) contribute to the mobility, it is difficult to extract hole-phonon interaction constants from DC transport measurements. It is usually more reliable to determine these coupling constants from optical measurements [4,5,21] or calculate them using *ab initio* [22,23] or semiempirical [24] methods.

The squared matrix element for nonpolar hole-optical phonon scattering is given by [10,20,26]

$$|V(\vec{q})|^2 = (D_t K)^2 u_{\vec{q}}^2 \; = \; \frac{\hbar (D_t K)^2}{2V_0 \rho \omega} \left(N_{\vec{q}} + \frac{1}{2} \pm \frac{1}{2} \right), \tag{1}$$

where $(D_t K)$ is the optical deformation potential constant for holes, $u_{\vec{q}}$ the rms amplitude of an optical phonon, V_0 the volume of the crystal, ρ its density, and $\hbar\omega$ the optical phonon energy (assumed constant). $\vec{q}$ is the wave vector of the phonon and $N_{\vec{q}}$ its occupation number. In the Pikus-Bir notation [10], the optical deformation potential for holes is $d_0 = a\,(D_t K)\sqrt{\frac{2}{3}}$, where a is the lattice constant. The value of $(D_t K)$ or d_0 has long been a source of controversy. The transport community [18] has been using d_0=46 eV, but lower values between 30 and 35 eV were found from the broadening of the Raman line in p-type Ge [21]. The most reliable (i.e., using first-principles methods) calculated values [22–24] are also in the same range. Using the linear muffin-tin orbitals (LMTO) method within the atomic sphere approximation (ASA), Brey *et al.* [22] found d_0=29.3 eV, if a correction to the straight LMTO-ASA result (d_0=22.4 eV) is made to account for the internal strain. Preliminary results for GaAs and Si [25] using the full potential LMTO method (which handles nonspherical symmetries more accurately than LMTO-ASA) agree with the LMTO-ASA results up to 10%. A pump-probe transmission experiment [4] in p-type Ge using 1 ps pulses at 10 μm was interpreted with d_0=42 eV. A subsequent femtosecond experiment by the same group [5] is described with d_0=30 eV. Part of the confusion about the value of d_0 may be due to the p-type nature of the hole wave functions, which is sometimes taken into account by multiplying the squared matrix elements with an overlap factor of $\frac{1}{2}$. In this work, the hole wave functions are calculated with the $\vec{k}\cdot\vec{p}$-method, therefore no overlap factors are necessary.

In order to study the light hole to heavy hole scattering in Ge and determine the optical deformation potential d_0 for holes, we have measured the transient reflectivity changes ($\Delta R/R$) of intrinsic Ge at 300 K using 140 fs pulses from a commercial titanium-sapphire laser. A strong pump pulse (180 mW, 40 μm radius, 85 MHz repetition rate) is focussed onto a bulk Ge crystal and creates a surface carrier density [27] of about 4×10^{18} cm^{-3}. The reflectivity of a weaker probe pulse (near normal incidence) is measured in the standard slow-scan pump-probe geometry using two choppers and three lock-in amplifiers. The relative reflectivity change ($\Delta R/R$) as a function of delay time τ is shown by the thick solid line in Fig. 1 (a). At small negative time delays, there is a small increase in the reflectivity followed by a sharp drop which peaks near 0.3 ps. The reflectivity then recovers within about 6 ps.

The reflectivity changes measured here are mostly due to the photoexcited carriers (created by the pump pulse) performing plasma oscillations at the probe laser frequency ω_L, thus screening the electric field of the probe laser. Within the Drude model [28], the change to the dielectric function ϵ due to the free carriers can be calculated. In the high-frequency limit, it depends only on the sum of the ratios of the carrier density n to the respective effective mass m in all electron valleys (e) and hole bands (h),

$$\Delta\epsilon\left(\omega_L,\tau\right) = -\epsilon_s\frac{\omega_P^2\left(\tau\right)}{\omega_L^2}, \tag{2}$$

$$\omega_P^2\left(\tau\right) = \frac{e^2}{\epsilon_s\epsilon_0}\left[\sum_e\frac{n_e\left(\tau\right)}{m_e}+\sum_h\frac{n_h\left(\tau\right)}{m_h}\right], \tag{3}$$

where ϵ_s is the DC dielectric constant and ω_P the plasma frequency. Since the relaxation rate of the plasma oscillations is small compared to the laser frequency, the damping is weak, and the resulting change to the imaginary part of ϵ can be neglected. Therefore, the plasma oscillations cannot be observed in a pump-probe transmission experiment [9], which primarily measures the imaginary part of ϵ. The resulting change of ϵ_1 has been determined previously by Choo *et al.* [7]. Once $\Delta\epsilon$ is known, the reflectivity change ΔR can be calculated. The small spatial dependence of the dielectric function (due to the vertical carrier density profile) can be neglected.

We use the results of an ensemble Monte Carlo simulation described elsewhere [26] to model the experimental data. The electron and hole concentrations as a function of delay time τ are shown in Figs. 5 and 7 of Ref. [26]. Electrons are created in the Γ-valley. They initially scatter to the satellite valleys (predominantly the X-valley because of its higher density of states) within 100 fs. After about 4 ps, most electrons have relaxed to the bottom of the X-valley and then have scattered to the L-valley, which is the global minimum in Ge. The Monte Carlo simulation shows that 25% of the holes are created in the light hole band. They scatter to the heavy-hole band with a time constant of about 1 ps, which can easily be resolved with our 140 fs laser pulse. This time constant of 1 ps is much longer than the lifetime of Γ-electrons [6,8,9]. The simulations were performed for conditions similar to the experiment (1.5 eV pulses with a half-width of 100 fs, surface carrier density 10^{18} cm^{-3}), but diffusion and band gap renormalization were not included. We can scale the Monte Carlo results by a factor of 4 to obtain results for n=4×10^{18} cm^{-3}, since the scattering rates are approximately linear in density, at least for a small range of densities. (This has been confirmed by performing simulations at different densities.) Because of the large density of states at X and L in Ge, Pauli blocking does not affect the electrons as much as Γ-electrons in GaAs, at least not for our photon energy (1.5 eV) high above the direct gap.

Figure 1 (b) shows the contributions to the Drude reflectivity from the electrons and holes in different bands (calculated from the Monte Carlo densities). It can clearly be seen that the peak at 0.2 ps is due to the occupation of the light hole band and not the Γ-electrons, which scatter to the satellite valleys on a much faster time scale [6,8,9]. The peak decreases, as the light holes scatter to the heavy hole band. The slow increase after 1 ps is due to the scattering of electrons from the X-valleys to the L-valleys. The total calculated transient Drude reflectivity [thick solid line in Fig. 1 (b)] is compared with the experimental data in Fig. 1 (a). The agreement (although qualitatively OK) is not good, since we have not yet corrected the Monte-Carlo densities to account for diffusion and band gap renormalization.

Corrections due to diffusion were calculated by solving the diffusion equation

$$\frac{\partial n}{\partial t} = D(t)\frac{\partial^2 n}{\partial x^2} - \lambda n + g(x,t) \tag{4}$$

with a time-dependent diffusivity $D(t)$. λ is the bulk recombination rate. The dominant recombination process [1] at $n = 4 \times 10^{18}$ cm^{-3} is Auger recombination with a time constant of 625 ns. $g(x,t)$ describes the generation of cariers by the laser. The initial and boundary conditions are

$$n(x,t) = 0 \quad \text{at} \quad t = -\infty, \tag{5}$$

$$\frac{\partial n}{\partial x} = 0 \quad \text{at} \quad x = 0. \tag{6}$$

The diffusivity as a function of carrier and lattice temperature (T_c and T_L, respectively) is given by Smirl [1]:

$$D(t) = D_0 T_L^{-1} \sqrt{T_c}, \tag{7}$$

where the ambipolar diffusivity at 300 K is D_0=67 cm^2/s. The average carrier temperature T_c can be obtained from the energy distribution in all six electron and hole bands found in the Monte Carlo simulation. The reflectivity calculated from the Monte-Carlo densities, corrected for diffusion, are given by the dotted line in Fig. 1 (a). We see that diffusion gives an important correction to $\Delta R/R$.

Finally, we consider reflectivity changes due to band gap renormalization (BGR) using Zimmermann's model [16]:

$$\Delta E_g = -\frac{3.24 r_s^{-3/4}}{(1 + 0.0478 r_s^3 \theta^2)^{1/4}} E_{\text{exc}}, \tag{8}$$

where r_s is the (dimensionless) interparticle separation measured in terms of the excitonic Bohr radius a_B, $\theta = kT_c/E_{\text{exc}}$ the reduced temperature, and E_{exc} the exciton binding energy. Since the reflectivity change at 1.5 eV is mostly due to the renormalization of the E_1 critical point, we should use the binding energy and Bohr radius of the E_1 exciton [29]. Since these values are not well known, we use the parameters of the indirect exciton, which seem to yield reasonable renormalization energies. (Using the direct exciton parameters also results in similar values.) The carrier temperature T_c was again taken from the Monte Carlo simulation [26]. Once ΔE_g is known, the reflectivity change can be calculated from the energy dependence of the dielectric function [27]. We also have to consider the fact that only about 99% of the carriers from a given pump pulse diffuse or recombine before the arrival of the next pump pulse. Under steady-state conditions, with repetitive pump pulses, this leads to a background carrier accumulation of about 20% of the maximum carrier density. (This number can be obtained by solving a steady-state diffusion equation containing an Auger recombination term.) The resulting BGR corrections are given by the dashed line in Fig. 1 (a). The thin solid line gives the reflectivity calculated with our final model, including carrier dynamics, diffusion, band gap recombination, and carrier accumulation.

We stress that the comparison between theory and experiment in Fig. 1 (a) contains only one fit parameter: The spot size of the pump laser. The agreement can be improved by fine-tuning the Auger recombination rate (at late times) and the optical deformation potential for holes. The positive peak at negative time delays was also observed in Ref. [9] and attributed to BGR effects. However, our simple BGR model was unable to account for this peak. Most likely, this peak is due to the population of electrons in the Γ-valley within the first 100 fs.

In summary, we have measured the transient reflectivity changes ($\Delta R/R$) in bulk intrinsic Ge using 140 fs laser pulses. The observed spectrum can be explained well by calculating the Drude response of the photoexcited carriers (taking into account diffusion into the bulk). Band gap renormalization as well as carrier accumulation also need to be considered. Using the unique band structure of Ge and an experimental reflectivity (not transmission) technique, we are able to isolate the dynamics of the holes in a femtosecond pump-probe experiment. The Monte Carlo simulation (which uses an optical deformation potential for holes of d_0=46 eV) overestimates the scattering rate of light holes to the heavy hole band. The agreement can be improved when a lower value determined from a line shape analysis of the Raman line in p-type Ge (between 30 and 35 eV) is used [21].

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References

[1] A. Smirl in *Semiconductors Probed by Ultrafast Laser Spectroscopy*, ed. R.R. Alfano (Academic, Orlando, 1984), Vol. 1, p. 197.

[2] J.F. Young and H.M. van Driel, Phys. Rev. B **26**, 2147 (1982); M.I. Gallant and H.M. van Driel, *ibid.* **26**, 2133 (1982); A. Othonos, H.M. van Driel, J.F. Young, and P.J. Kelly, *ibid.*, **43**, 6682 (1991).

[3] H. Roskos, B. Rieck, A. Seilmeier, and W. Kaiser, Appl. Phys. Lett. **53**, 2406 (1988).

[4] M. Woerner, T. Elsaesser, and W. Kaiser, Phys. Rev. B **41**, 5463 (1990).

[5] M. Woerner, W. Frey, M. T. Portella, C. Ludwig, T. Elsaesser, and W. Kaiser, Phys. Rev. B **49**, 17007 (1994); M. Woerner and T. Elsaesser, *ibid.* **51**, 17490 (1995).

[6] T. Rappen, U. Peter, W. Wegener, and W. Schäfer, Phys. Rev. B **48**, 4879 (1993).

[7] H.R. Choo, X.F. Hu, M.C. Downer, and V.P. Kesan, Appl. Phys. Lett. **63**, 1507 (1993).

[8] X.Q. Zhou, H.M. van Driel, and G. Mak, Phys. Rev. B **50**, 5226 (1994); X.Q. Zhou and H.M. van Driel, QELS '93 Technical Digest, p. 247.

[9] G. Mak and H.M. van Driel, Phys. Rev. B **49**, 16817 (1994); Proc. SPIE **2142**, 120 (1994).

[10] L. Reggiani, *Hot-Electron Transport in Semiconductors*, (Springer, Berlin, 1985).

[11] C.J. Stanton and D.W. Bailey, in *Monte Carlo Device Simulation: Full Band and Beyond*, edited by K. Hess, (Kluwer, Boston, 1991), p. 67.

[12] J. Shah and R.F. Leheny in *Semiconductors Probed by Ultrafast Laser Spectroscopy*, ed. R.R. Alfano (Academic, Orlando, 1984), Vol. 1, p. 45.

[13] X.Q. Zhou, K. Leo, and H. Kurz, Phys. Rev B **45**, 3886 (1992); A. Chébira, J. Chesnoy, and G. M. Gale, *ibid.* **46**, 4559 (1992); A. Tomita, J. Shah, J.E. Cunningham, S.M. Goodnick, P. Lugli, and S.L. Chuang, *ibid.* **48**, 5708 (1993); R. Tommasi, P. Langot, and F. Vallée, Appl. Phys. Lett. **66**, 1361 (1995).

[14] D.K. Ferry, M.A. Osman, R. Joshi, and M.-K. Kann, Solid-State Electron. **31**, 401 (1988).

[15] M. Combescot, Solid-State Electron. **31**, 657 (1988).

[16] R. Zimmermann, phys. stat. solidi (b) **146**, 371 (1988).

[17] H. Kalt and M. Rinker, Phys. Rev. B **45**, 1139 (1992).

[18] J.D. Wiley in *Semiconductors and Semimetals*, edited by R.K. Willardson and A.C. Beer, (Academic, New York, 1975), vol. 10, p. 91.

[19] M.V. Fischetti and J.M. Higman, in *Monte Carlo Device Simulation: Full Band and Beyond*, edited by K. Hess, (Kluwer, Boston, 1991), p. 123.

[20] E.M. Conwell, *High Field Transport in Semiconductors*, (Academic, New York, 1967).

[21] F. Cerdeira and M. Cardona, Phys. Rev. B **5**, 1440 (1972); D. Olego, Ph.D. thesis (unpublished).

[22] L. Brey, N.E. Christensen, and M. Cardona, Phys. Rev. B **36**, 2638 (1987).